ALPHA-GAMMA
TECHNOLOGIES, INC.

MEMORANDUM:

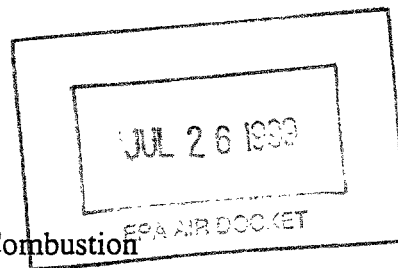**DATE:**   June 26, 1996

SUBJECT: Search of Dissertation Abstracts for Natural Gas Combustion

FROM: James Camp
              Alpha-Gamma Technologies, Inc.

TO: Combustion Turbines and RICE NESHAP Project Files

Search String: "Natural Gas Combustion"
Hits:
        Studies in Atmospheric Chemistry: 1. Primary Peroxides from Hydrocarbons. II. Elemental Analysis Using Nuclear Reactions. AU: McKinney, Peter Michael. Vol 45-09B Dissertation Abstracts International, pg 2893, NO AAI8427044.
 (Attached)

Search String "Combustion"

        Theoretical and Experimental Studies of Unimolecular Reactions Relevant to Combustion and the Atmosphere. Stewart, Paul Hendry. Vol 52-10B of Dissertation Abstracts International, pg 5278, NO AAIDX94823.
(Attached)

        Optimal Hypergolic (compression ignition) Combustion In An Internal Combustion Engine. Min, Young Ke, Vol 47-12 B of Dissertation Abstratcts International, Pg 5029, NO AAI8708513.
(Not relevant)

        Preignition Oxidation Characteristics of Hydrocarbon Fuels (Autoignition, Kenetics, Combustion Chemistry). Wilk, Richard David, Vol 47-04B Dissertation Abstracts International, pg 1687, NO AAI8616270.
(Attached)

        Theoretical and Experimental Investigation of Methanol Combustion Under Constant Volume. Tatum, Patricia Anne Faison, vol 45-01B of Dissertation Abstracts International, pg 213, NO AAI 8410493.
(Very Low Relevance)

Chemical Characterization of Combustion Products of Number 2 Fuel Oil. Leary, Julie Ann, Vol X1984, NO AATO369589.
(Could not find Vol X1984)

Search String "Formaldehyde Formation"

Engine Operating Parameter Effects on Speciated Aldehyde and Ketone Emissions From A Natural Gas Fuelled Engine. Crawford, John Gordon, Vol 34-02 of Dissertation Abstracts International, p 807, NO AAIMMO1988.
(Could not find in Vol 34)

Search String "Formaldehyde Emissions"

Time-Resolved Exhaust Port measurements of Unburned Fuel and Aldehyde Emissions From a Methanol-Fuel Texaco L-1635 TCCS Engine. Kim, Chang Ho, vol 46-07B Dissertation Abstracts International, NO AAI8513462.
(Could not find Vol 46-07B)

DETECTING AND LOCATING DAMAGES IN COMPLEX STRUCTURES BY THE SYSTEM IDENTIFICATION TECHNIQUE
Order No. DA8614296

WEN-HU, PH.D. *University of Maryland*, 1985. 234pp. Director: Professor C. S. Yang

Two new methods of identifying crack locations in complex, continuous structural systems by investigating the changes in the stiffness and flexibility matrices are presented. These two matrices can be obtained by applying the System Identification Technique to the measured dynamic response of the system under either impulse or random forcing function. Theoretically, the above two matrices can also be obtained by the finite element method and system reduction technique if the real damage size in the structure is known. Initially, analyses by the finite element method are made for cases with several different crack locations and boundary conditions in a steel beam. An experiment using an aluminum beam with different size cracks has also been conducted to verify the proposed technique. Similarly, the finite element models of a square plate with hole or crack damage and 1/4 scale offshore platform with a through cut in one secondary horizontal member were analyzed.

Simplicity in both on-site measurement and analysis makes the technique particularly useful for real time applications.

—

CONTROL OF A MULTI-SEGMENT BI-STABLE MANIPULATOR
Order No. DA8613227

TSUKAMAKI, TAKASHI, PH.D. *University of Washington*, 1985. 262pp. Chairperson: Joseph L. Garbini

The control of a manipulator consisting of multiple segments whose joints have only bi-stable positions is described. The inverse transformation named "Flip Transformation," which maps the spatial coordinates in the workspace into the joint coordinate bi-stable states, is developed for this manipulator. Two modes of operation provide (1) Point-To-Point and (2) Pattern Propagation for the manipulator motions. Primitive coordinated motions are introduced in the binary regression technique for the first mode and the overall synchronized movements are constructed only with those primitives. Control algorithms for a snaking motion (second mode), over or round an obstacle, are accomplished by the binary proportional-integral-derivative control technique.

The design concept for the manipulator is based on many modularized identical segments connected to each other in series. Individual segments are controlled to a bi-stable position. By incorporating a sufficient number of segments and properly deflected joints, a flexible and dexterous manipulator could be realized, and the desired manipulator end link position in the workspace as well as the total shape of the manipulator can be obtained.

Previous solutions for the inverse transformation of the bi-stable multi-segment manipulator system have not been effective, and a solution with efficient and direct algorithms is desirable. Methods developed in the past have initiations such as excessive computational time, limited convergence in an optimal solution, arbitrarily selected parameters, transformation only in a specific configuration, etc. Consequently, the time required to compute the algorithms as well as the solution itself may not have been optimal.

An inverse transformation ("Flip Transformation") has been developed and utilized to solve this problem analytically and efficiently for a system with large degrees of freedom (many segments). The transformation is accomplished by a properly sequenced geometric mapping that converts the mirror image representations of the manipulator section into the equivalent binary number complement algorithms. The solution of the joint variables (states) is sought as a binary number in which each digit represents an individual joint state.

Controls of the manipulator motion are derived from optimization algorithms based on minimum energy criteria, and smooth transitional movements can now be realized by minimizing the C.G. motions for each joint state change. The primitive motions are identified and utilized with a hierarchical priority order to obtain the comprehensive overall manipulator movements.

LASER DOPPLER MEASUREMENTS OF GRID TURBULENCE IN A BOX
Order No. DA8616013

WALKER, MICHAEL DEAN, PH.D. *The Johns Hopkins University*, 1986. 130pp.

The decay of grid-generated turbulence was measured for long decay times, $U_G t/M < 1900$, for moderately high mesh Reynolds number, $R_M = 1.7 \times 10^4$. The grid moved vertically at constant speed through water in a tank. Measurements were made with a frequency-shifted laser Doppler velocimeter with a tracker. Ensemble averaging was used to obtain the velocity moments for the streamwise and transverse components.

Before data could be taken, four problems were identified and corrected. These were: tracker drift, tracker harmonic intermodulation, failure of the signal validation at small velocity, and temperature stratification of the tank. In previous LDV measurements of turbulence, measurements were limited to turbulence intensity greater than 1%. Here, with the above problems avoided, measurements as small as 0.04% of the grid speed were achieved.

The measurements of the turbulence decay were compared to previous measurements. Both u' and v' decay agreed with the extrapolated curvefits of the data measured by Corrsin (1942). Perhaps more surprising, at large $U_G t/M$ the decay data also agreed with the extrapolated curvefits of data taken at 0.34 solidity, without any adjustment to account for the difference in solidity. For small $U_G t/M$, the u'/v' ratio was in rough agreement with earlier hot-wire measurements, viz. $u'/v' \simeq 1.3$. For large $U_G t/M$, u'/v' decreased, and became approximately unity at $U_G t/M = 1500$. Finally, preliminary results may indicate an approach to a linear decay, i.e. $U_G{}^2/v'^2 \propto U_G t/M$ for $300 < U_G t/M < 10^4$. The absolute accuracy of the velocity data was limited by the accuracy of the fringe spacing measurement, about $\pm 0.6\%$. The data uncertainty was governed by the number of realizations in the ensemble, 256 for most of the data.

SPINNING SELF-FORGING FRAGMENTS AND SHAPED CHARGES
Order No. DA8616268

WEICKERT, CHRIS ALLEN, PH.D. *Drexel University*, 1986. 229pp. Adviser: Pei Chi Chou

This thesis is concerned with the application of fluted-liner technology to spinning self-forging fragments and shaped charges. Historically, shaped charge fluted liner research consisted of experimental parametric studies. The actual mechanism of spin compensation was not understood.

Numerical results from the current research on the collapse of fluted shaped charge liners show that the explosive gases rotate in one direction but the jet and slug rotate opposite to each other with the net result being opposite to that of the explosive gases. Numerical calculations were used to predict the variation of angular momentum of the shaped-charge liner with the number of flutes and with the index angle. As the number of flutes is increased, the direction of rotation of the jet changes from clockwise to counter-clockwise. The reversals in spin direction from experiments are duplicated by the numerical results.

Results from an experimental investigation of a spinning self-forging fragment have demonstrated for the first time that a spinning cohesive fragment could be formed with a backward-folding liner design at an SFF charge spin rate of 2500 RPM.

PREIGNITION OXIDATION CHARACTERISTICS OF HYDROCARBON FUELS
Order No. DA8616270

WILK, RICHARD DAVID, PH.D. *Drexel University*, 1986. 237pp. Advisers: Nicholas P. Cernansky, Richard S. Cohen

Studies of the preignition oxidation characteristics of hydrocarbon fuels have been conducted. Experimental results obtained from a static reactor are presented for the oxidation of a variety of fuels. Pressure and temperature histories of the reacting fuel/oxidizer mixtures were obtained. Measurements of the stable reaction intermediate and product species were made using gas chromatographic analysis.

One aspect of this work involved detailed studies of the oxidation chemistry of relatively low molecular weight aliphatic hydrocarbons: propane, propene and n-butane. The oxidation chemistry of these

fuels was examined at temperatures in the range 550-750 K, equivalence ratios ranging from 0.8 to 4.0 and at subatmospheric pressures. The experimental results for each of these fuels indicate a clear transition in the oxidation chemistry for a low temperature regime to an intermediate temperature regime, separated by a region of negative temperature coefficient. The transition occurs between approximately 600 and 700 K. The main characteristics and features of the oxidation mechanisms were determined for each fuel in each temperature regime.

Chemical kinetic modeling of propene and propane oxidation at low and intermediate temperatures was conducted in cooperation with Lawrence Livermore National Laboratory. The experimental results from propene and propane were used to develop a low and intermediate temperature kinetic mechanism for these fuels based on a low temperature acetaldehyde mechanism of Kaiser et al. and a high temperature propene/propane mechanism of Westbrook and Pitz. Comparison of the predicted results of the chemical kinetic model with the experimental results shows reasonable agreement.

Another aspect of this work involved studies of the general preignition characteristics of higher molecular weight hydrocarbons and binary mixtures of these fuels. The low temperature/cool flame ignition characteristics of dodecane were investigated at temperatures in the range 523-623 K, equivalence ratios ranging from 0.8 to 1.0 and at subatmospheric pressures. The effects of initial conditions on the cool flame induction period and pressure rise were determined. The preignition characteristics of binary mixtures of dodecane and the aromatic component tetralin were examined. The addition of the tetralin had the overall effect of decreasing the ignition tendency of the mixture, although this effect was nonlinear with respect to the amount of tetralin added.

SYSTEMS DESIGN OF A WALKING ROBOT

Order No. DA8611444

WONG, TIN-LUP. PH.D. *The University of Wisconsin - Madison*, 1986. 231pp. Co-Supervisors: N. H. Beachley, A. A. Frank

A feasibility study of a walking robot that can run at about 30 mph was explored using the systems design methodology. Systems Engineering is not a monopoly of large scale systems. It can be applied to any system, independent of its size; the real spirit of the methodology is to conduct systems synthesis and analysis so as to create appropriate system configurations with satisfactory performance and decide among the candidate systems.

To provide enough independently controllable degrees of freedom in each leg for terrain adaptivity, robot legs are generally high-speed spatial mechanisms. The dynamic forces that a robot leg creates will have a considerable effect on the moving base, this led to the consideration of three different approaches for the solution of the problem.

The first approach investigated was the possible kinematic design alternatives. The second approach considered was the use of composite materials for the fabrication of lightweight robot legs, which gives the advantages of better weight and inertia properties.

Finally a general approach to the minimization of dynamic forces of mechanisms has been formulated, which makes use of the matrix method for the analysis of mechanisms and a heuristic optimization technique for the minimization of the undesirable inertia forces. A general computer program BALANC was written for the illustration of the method as well as for general applications.

NUMERICAL MODELS FOR FLOW AND SEDIMENT TRANSPORT DYNAMICS IN DEEP OCEAN TURBULENT BOUNDARY LAYER

Order No. DA8613683

YEAN, JUNGTSUN. PH.D. *University of California, Santa Barbara*, 1985. 150pp. Chairman: Stephen McLean

The main purpose of this research is to present theoretical models simulating the cogent physical processes acting in the deep ocean boundary layer and to develop the corresponding numerical methods for predicting the turbulent flow field as well as estimating the sediment transport. The paper commences with an investigation of the structure of deep ocean benthic boundary layer flow. Particular emphasis is placed on a time and space dependent eddy viscosity to relate Reynolds stress with the mean velocity gradient in the momentum equation of turbulent flow. The second part of the

dissertation then looks at the sediment response to the regime within the boundary layer.

The present numerical method used to solve the equation is to directly compute the vertical structure of amplitude of the velocity field within the benthic bound through a finite difference method. The results show go with the field measurements of flow velocities and Reyn and provide needed information concerning flow mech for estimates of suspended sediment transport.

The flow factors having direct bearing on sediment t the shear stress induced from turbulent flow on the sea eddy diffusivity within flow field. The former initiates the motion by eroding the sea bed materials, the latter diffu eroded particles into water column and produces mixin turbulent eddies.

The computation of sediment concentration is base integral of volume concentration with respect to particle distribution, which allows a more reasonable evaluation all sizes involved in sedimentation. The model proposed transport process consists of four aspects: (1) erosion; and diffusion; (3) aggregation and disaggregation; (4) log-normal distribution of particle volume distribution is erosion rate, in order to initiate the computation of parti frequency. The model results indicate that aggregation disaggregation are not important for short time period.

COMPUTER-AIDED OPTIMIZATION IN THE DYNA ANALYSIS AND PARAMETRIC DESIGN OF ROBO MANIPULATORS

Order No.

YUAN-CHOU, HSIN-CHIEN, PH.D. *The University of Florida* Chairman: Delbert Tesar

Robotic manipulators provide general, programable and force functions to carry out highly dextrous and flex processes. These systems are characterized by several freedom of controllable motion. As a consequence, the mechanical structure contains a very large number of de including geometric, mass, stiffness, strength and actua parameters. The mathematical relations between the pa the manipulator's force and motion states are extraordin complex, nonlinear, and highly coupled. Therefore, the manipulators is an expensive, time-consuming, and cha Presently, the designers are lacking guidelines and well design criteria.

This study brings together two fields: optimization the robotics. The goal is to develop analysis, design criteria computational tools for optimizing the distribution of act parameters which satisfy load and precision requiremen increase the system's fundamental natural frequency for operations.

A rigid-link manipulator model is employed in this stu generated plots are used to display extensive analysis in compact, understandable form. These plots show how sy parameters vary as a function of hand position. Compute procedures for systems become an imperative in order to the dynamic design formulation, select rational design sp and evaluate the system's operating characteristics both globally.

In order to develop a first level of computational and o methodology, local properties, i.e., properties at a specif configuration of the device, are considered first. A more methodology would result by considering a range of con the workspace. This leads to the application of general m optimization techniques to develop design tools for man design techniques developed here can greatly reduce th cycle time for accurate, reliable manipulators, and also b improve or redesign existing manipulators to produce be performance. A detailed analysis for the industrial robot presented.

irogen atom transfers and
ns. Part II. Asymmetric
art III. Total synthesis of
a radical cyclization. Shen,
1991. 252pp.
Order Number DA9209365
y radical reaction, 1,5-hydrogen
sation, was described in this part.
monoalkylthio, dialkylthio, thio-
ester, nitrile, tertiary, secondary,
he transferring C-H bonds were
a was first to generate vinyl rad-
carbon centers by 1,5-hydrogen
radical cyclizations. Stork's cat-
ition of tin hydride method, and
used to run the radical reactions,
st substituents gave compatible
(generally 50–100% vinyl radicals
ers), except for some strong C-H
ransfer (for epoxide and methyl).
ed the C-H bonds best, however,
adicals attacking the sulfur atoms
red with the desired 1,5-hydrogen
n labeling experiments, we found
is the rate determine step in the

n radical chemistry was reported
im was used as the chiral auxiliary
radical additions to allylstannane
reoselectivities even at 25°C or
ompatible with the alkylation of
l cylizations with the same chiral
lectivities at α position, but poor
the β position. The chiral radical
the system.

atural product, modhephene was
ie framework of modhephene was
one step via a novel tandem radi-
is. This process, the transannula-
l the following radical cyclization,
In the course of our synthesis, we
onversion from a common inter-
nodhephene and epimodhephene.
> yield in 22 steps from commer-
il, while epimodhephene was ob-
t. The total yield for both mod-
4%.

isted excited singlet states
on. Shin, Kwansoo, Ph.D. The
Major Professor: Edwin F. Hilin-
Order Number DA9209133
>y permitted the direct detection
$^{1}p^{*}$) of several polyarylethylenes

ylene (TPE) supported the in-
in terms of overlapping spectra
[$^{+}$) and the diphenylmethyl an-
stants of $^{1}p^{*}$ were (2.3 ± 0.3)
± 1.0) × 10^{9} s^{-1} in THF, and
.te. A straight line resulted from
rate constant vs. the empirical

E) exhibited a λ_{max} at 430 nm.
han 20 ps.
etra(p-anisyl)ethylene (TAE) in
CN showed two absorption max-
ctronic structure of the $^{1}p^{*}$ was
. The lifetimes of these maxima
is in cyclohexane, and <20 ps in
itrile.
nylethylene (DADPE) in cyclo-
ima at 445 nm and 480 nm. The

electronic nature of the $^{1}p^{*}$ of DADPE was also explained as a zwit-
terionic state. The lifetime of the $^{1}p^{*}$ was 35 ± 10 ps in cyclohexane
and <20 ps in tetrahydrofuran.
Picosecond-pulsed irradiation of tetra(p-cyanophenyl)-ethylene
(TCE) was carried out in cyclohexane, THF, CHCl$_3$, CH$_2$Cl$_2$, and
CH$_3$CN. Two absorption maxima appeared at 450 nm and 500 nm in
CHCl$_3$, and at 445 nm and 485 nm in CH$_2$Cl$_2$. One λ_{max} at 480 nm
appeared in solution of cyclohexane, THF, and CH$_3$CN. The lifetimes
of the $^{1}p^{*}$ were ~750 ps in cyclohexane, 25 ± 10 ps in THF, 215 ± 20
ps in CH$_3$Cl, 90 ± 25 ps in CH$_2$Cl$_2$ and <20 ps in acetonitrile.
Other polyarylethylenes were also subjected to picosecond-pulsed
excitation. For these molecules, no significant time-resolved absorption
spectra were observed in the spectral range from 370 nm to 810 nm from
the time of excitation to 20 ns postexcitation.

Langmuir-Blodgett films of some novel phthalocyanines.
Simmons, John M. Ph.D. *University of East Anglia (United Kingdom)*,
1991. 253pp. Order Number BRDX94741
*Available from UMI in association with The British Library. See inside back
cover for order information.*
Phthalocyanines are an important industrial commodity used pri-
marily as inks, colourings for plastics and dyestuffs used in the cloth-
ing industry. More recently, interest has centred on less passive uses of
these materials, exploiting their interesting electrical and optical prop-
erties. Thus future potential applications of phthalocyanines include
electrochromic display devices, photosensitising reagents in cancer ther-
apy, laser dyes and liquid crystal display applications.
The work in the thesis was formulated with two principal aims in
mind. The first was the development of a range of highly soluble ph-
thalocyanine derivatives with Q-band absorbances in the near infrared
region of the spectrum. The second was more specific and was con-
cerned with producing thin films of the materials using the Langmuir-
Blodgett (LB) technique.
The synthesis and characterisation of the materials are described in
chapter 2. Chapters 3 and 4 explore the monolayer and deposition
properties of a number of phthalocyanines and the molecular ordering
within the deposited films is discussed with reference to a variety of
physical techniques including x-ray diffraction, polarised visible and
infra-red spectroscopy.
A further aspect of this work concerned the use of an ultra thin LB
film of a phthalocyanine as a sensing element in an acid sensor. The
response of phthalocyanine films to various acid vapours, measured in
terms of sensitivity, selectivity, reversibility and recovery after expo-
sure, is discussed in chapter 5.

Theoretical and experimental studies of unimolecular re-
actions relevant to combustion and the atmosphere. Stew-
art, Paul Hendry, Ph.D. *University of Aberdeen (United Kingdom)*, 1986.
402pp. Order Number BRDX94823
*Available from UMI in association with The British Library. See inside back
cover for order information.*
The pyrolysis of methyl nitrite (1 torr) in the presence of nitrogen
dioxide (1 torr) was studied at 458K over the pressure range 0–760
torr of carbon tetrafluoride. The only detectable products were methyl
nitrate and formaldehyde.
The pyrolysis of perfluoroazo-2-propane, PAP, (25 torr) was studied
over the temperature range 450–514K. The products were nitrogen and
perfluorohexane, PFH, which were produced in equal amounts. The
production of nitrogen was found to be first order with respect to the
azo compound. First-order kinetics were observed even for extents of
reaction exceeding 60%. No surface effects were observed. The reaction
was pressure independent.
The pyrolysis of formaldehyde (4–10 torr) was studied using a static
system over the temperature range 705–773K and 150–760 torr of car-
bon dioxide. Methane (4–10 torr) was used as an inert marker. Pre-
liminary experiments showed that methane did not decompose under
these experimental conditions. The only measurable products were hy-
drogen and carbon monoxide. No pressure dependence was observed,
even at the highest temperatures studied.
The decomposition of the trifluoromethoxy radical was examined
using an RRKM model, reconciling the calculated parameters for this
radical with the pressure dependent data of Descamps and Forst ob-
tained at 532.8K.

The RRKM parameters obtained from the
methoxy radical were then used as a base
endent falloff for the similar methoxy radi
The RRKM program used to model the pre
ions was also used to model the experime
of Batt and Robinson for the decompositi
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A similar study to that outlined for the t-I
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The pressure dependent combination of C
O$_2$, where CX$_3$ = CF$_3$, CH$_3$, CCl$_3$ an
oom temperature using the RRKM prog
nstant relating the reverse decomposition s
Abstract shortened by UMI.)

New synthetic methods involving alle
Massachusetts Institute of Technology, 199
heiser
Part one of this thesis describes a new "on
hod for the synthesis of highly substituted
of allenylsilanes with acylium ions (genera
induced decomposition of acyl chlorides)
vergent and allows for the preparation of
stitution patterns including bicyclic deriv
an extension of several previously describe
ing annulations utilizing allenylsilanes and is
which allows for the preparation of five-membe
ounds. A study to further extend this methoc
rroles via the reaction of nitrilium ions and al
A new synthetic approach to the synthesis
cloreversion of alkylidene-β-lactones is repo
ork. Two examples of cycloreversion are re
oute to the precursor lactones. This previousl
forms the foundation for a triply-convergen
the synthesis of allenes. This strategy invol
rget allene into two carbonyl compounds a
ary work to achieve this strategy utilizing a
step is outlined. (Copies available exclusiv
14-0551, Cambridge, MA 02139-4307.
617-253-1690.)

Part I. The use of covalently attached
porphyrins in the remote site-selecti
teroids. Part II. The use of ionically
loporphyrins in the remote site-selecti
teroids. Stuk, Timothy Lee, Ph.D. *Indiana*
hairman: Paul A. Grieco Order
Part I. The use of covalently attached synt
the remote site selective hydroxylation of s
nese(III) tetraphenylporphyrins were attac
teroidal substrates via an ester linkage. These
catalyze the site-specific hydroxylation of un
tramolecular fashion with iodosylbenzene as
ample, a 6 × 10^{-4} M solution of 1 (n = 0)
chloride was treated with 10.0 equiv of iodosyl
ent hydrolysis of the ester tether afforded 2
Changes in the tether length (n = 0,1) and in
the steroid nucleus (C(3)-α, C(17)-β, and C
duce changes in the specificity of the hydrox
reases in yields were realized when 2,6-difl
re incorporated into the meso positions of th
Part II. The use of ionically coordinated synt
the remote site selective hydroxylation of
um manganese(III) tetraphenylporphyri
oidal sulfates and were oxidized with iodc
site specific hydroxylation of the steroid
ment of a 10^{-3} M solution of 3 in dega
equiv of iodosylbenzene afforded, af
yield of 4. Use of fluorinated porphyrins a
ses in yields. (Abstract shortened with p

the $^1p^*$ of DADPE was also explained as a zwit-
...etime of the $^1p^*$ was 35 ± 10 ps in cyclohexane
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... irradiation of tetra(p-cyanophenyl)-ethylene
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...ett films of some novel phthalocyanines.
Ph.D. *University of East Anglia (United Kingdom)*,
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*[in association with The British Library. See inside back
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...l experimental studies of unimolecular re-
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Ph.D. *University of Aberdeen (United Kingdom)*, 1986
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... methyl nitrite (1 torr) in the presence of nitroge-
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...formaldehyde (4–10 torr) was studied using a static
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...The pressure dependent combination of CX₃ with oxygen to form
...O₂, where $CX_3 = CF_3$, CH_3, CCl_3 and $CFCl_2$, was modelled
...room temperature using the RRKM program via an equilibrium
...tant relating the reverse decomposition step to the combination.
...(Abstract shortened by UMI.)

New synthetic methods involving allenes. Stoner, Eric John,
...D. *Massachusetts Institute of Technology*, 1991. Supervisor: Rick L.
...heiser

...Part one of this thesis describes a new "one pot" [3+2] annulation
...thod for the synthesis of highly substituted furans utilizing the reac-
...of allenylsilanes with acylium ions (generated in situ via the Lewis
...d induced decomposition of acyl chlorides). This method is highly
...vergent and allows for the preparation of a large number of furan
...stitution patterns including bicyclic derivatives. This annulation
...an extension of several previously described [3+2] five-membered
...annulations utilizing allenylsilanes and is part of a new strategy
...which allows for the preparation of five-membered heteroaromatic com-
...ounds. A study to further extend this methodology to the synthesis of
...oles via the reaction of nitrilium ions and allenylsilanes is described.
...new synthetic approach to the synthesis of allenes via the [2+2]
...cloreversion of alkylidene-β-lactones is reported in part two of this
...Two examples of cycloreversion are reported as well as a new
...te to the precursor lactones. This previously unreported cyclorever-
...forms the foundation for a triply-convergent reagent-based strategy
...the synthesis of allenes. This strategy involves disconnection of the
...allene into two carbonyl compounds and a thiol ester. Preli-
...work to achieve this strategy utilizing a Peterson olefination as a
...step is outlined. (Copies available exclusively from MIT Libraries,
...14-0551, Cambridge, MA 02139-4307. Ph. 617-253-5668; Fax
...253-1690.)

Part I. The use of covalently attached synthetic metallo-
porphyrins in the remote site-selective hydroxylation of
steroids. Part II. The use of ionically coordinated metal-
loporphyrins in the remote site-selective hydroxylation of
steroids. Stuk, Timothy Lee, Ph.D. *Indiana University*, 1991. 158pp.
Chairman: Paul A. Grieco   Order Number DA9203450

...P. I. The use of covalently attached synthetic metalloporphyrins
...the remote site selective hydroxylation of steroids: Synthetic man-
...ese(III) tetraphenylporphyrins were attached to several different
...steroidal substrates via an ester linkage. These porphyrins were shown
...catalyze the site-specific hydroxylation of unactivated carbons in an
...molecular fashion with iodosylbenzene as the oxygen source. For
...ample, a 6×10^{-4} M solution of 1 (n = 0) in degassed methylene
...ride was treated with 10.0 equiv of iodosylbenzene for 4 h. Subse-
...hydrolysis of the ester tether afforded 2 in 54% yield.
...anges in the tether length (n = 0,1) and in the site of attachment
...steroid nucleus (C(3)-α, C(17)-β, and C(17)-α) were shown to
...changes in the specificity of the hydroxylation site. Substantial
...ses in yields were realized when 2,6-difluorinated phenyl rings
...incorporated into the meso positions of the porphyrins.
...II. The use of ionically coordinated synthetic metalloporphyrins
...remote site selective hydroxylation of steroids: Trimethylam-
...manganese(III) tetraphenylporphyrins were coordinated to
...sulfates and were oxidized with iodosylbenzene. This gave
...specific hydroxylation of the steroid skeleton. For example,
...of a 10^{-3} M solution of 3 in degassed methylene chloride
...equiv of iodosylbenzene afforded, after acidic hydrolysis, a
...of 4. Use of fluorinated porphyrins again lead to substantial
...in yields. (Abstract shortened with permission of author.)

Zirconacyclopropanes
formation and reacti...
University, 1991. 205pp. M...

A convenient procedure
(1-butene), from Cp₂ZrCl...
ploration of the reactivity
zirconocene equivalent dis...
non-conjugated dienes by a...
clization. Alkenes and co...
carbometalation of the zir...
rated products.
The corresponding conju...
produced without incorpor...
conocene equivalent, Cp₂Z...
of t-BuLi. A facile π-displa...
a general synthesis of zirc...
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The decomposition of d...
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a non-dissociative mechani...
A convenient procedur...
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A novel mechanism for...
conocene catalyzed (Z)- t...
electron zirconocene inter...
proposed. The mechanistic

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CHEMISTRY

CHEMISTRY, GENERAL

AHARONOV-BOHM EFFECT AND NON-LOCAL PHENOMENA
Order No. DA8427745

LIANG, JIUQING, PH.D. *University of South Carolina*, 1984. 50pp.

Using the Feymann path integral method, a new interference experiment is analyzed under the classical limit. The results verify the Aharonov-Bohm effect. The general results of the AB interference experiment are consistent with the principles of quantum theory. The scattering of an electron by a magnetic field confined to an infinitely long penetrable and impenetrable solenoid with a finite radius demonstrates that the penetration of wave function into the solenoid cannot affect the results of the AB scattering. Also the non-local property of the AB scattering is demonstrated. The integral expression of two-dimensional partial wave scattering amplitude by a potential of cylindrical symmetry is derived. The Born series and the Born approximation of AB scattering are studied, and the nonvalidity of the Born approximation in the line-flux scattering is explored. The hydrodynamical approach to the AB effect is investigated, and it is found that the solution of the hydrodynamical equations is consistent with the Schrödinger equation. Also, the existence of the AB effect from the hydrodynamical formalism of quantum mechanics is explained.

STUDIES IN ATMOSPHERIC CHEMISTRY: I. PRIMARY PEROXIDES FROM HYDROCARBONS. II. ELEMENTAL ANALYSIS USING NUCLEAR REACTIONS
Order No. DA8427044

MCKINNEY, PETER MICHAEL, PH.D. *University of California, Berkeley*, 1984. 69pp.

In the first part the interaction of combustion effluents with gas phase SO_2 was studied in a cylindrical reactor. The apparent SO_2 concentration, as monitored by a fluorescence detector, was reduced 60 to 90% during propane combustion but only 10% during CO, natural gas or hydrogen combustion. The results were consistent with the formation of a gas phase sulfur species.

Peroxides were collected in a bubbler from the combustion effluent of methane, ethane, propane and butane. The peroxide concentration was greatest when the flame was interrupted (5 sec on/5 sec off), reaching a maximum concentration of 0.1 mole per 1000 moles of fuel. The peroxide concentration was lower for diffusion and premix combustion. These peroxides reacted rapidly with approximately 20 μM HSO_3^- forming SO_4^{2-}. More than 80% of the peroxides were H_2O_2. No peroxides were detected from natural gas combustion; most of the sulfur in the fuel was oxidized to SO_4^{2-}.

Exhaust from 3 different vehicles was also collected in the bubbler. A constant fraction of the sulfur, 25%, was oxidized to SO_4^{2-} in the bubbler water. The SO_4^{2-} concentration in the exhaust was several ppm, corresponding to several Img/min at idle. The exhaust from sulfur free iso-octane collected in the bubbler also reacted with HSO_3^- producing SO_4^{2-}. A concentration of peroxides comparable to the SO_4^{2-} was detected in the bubbler water, indicating the emission of primary peroxides from auto exhaust.

In the second part simultaneous analysis for C, N and O in atmospheric aerosols using charged particle activation analysis was attempted. Interference with the silver filter matrix prevented the determination of all three elements.

However using the $^{12}C(^3He,\alpha)^{11}C$ and $^{16}O(^3He,p)^{18}F$ reactions it was possible to simultaneously measure carbon and oxygen. The carbon results agreed with combustion within 15%. No comparison of the oxygen results was possible with an independent method, because other methods do not have the required sensitivity.

ANODIC STRIPPING VOLTAMMETRY AT A GLASSY CARBON ELECTRODE FOR THE DETERMINATION OF PLATINUM SPECIES DERIVED FROM CIS-DIAMMINEDICHLOROPLATINUM(II)
Order No. DA8429181

ATHERTON, DAVID REED, PH.D. *The University of Florida*, 1984. 286pp. Chairman: Gerhard M. Schmid

Following the administration of the anti-cancer drug cis-diamminedichloroplatinum(II), platinum is found throughout the body as a number of species. The lack of platinum deposition from untreated urine or from urine denatured with acetonitrile or mineral acids led to the use of chelation by sodium diethyldithiocarbamate followed by solvent extraction using chloroform to isolate the platinum from urine. Evaporation of the solvent and digestion of the residue in aqua regia was necessary to obtain a readily deposited form of platinum, chloroplatinic acid. Redissolution in a pH 1.7, 0.1 M bisulfate/sulfate solution resulted in both a strongly acidic buffer needed to prevent hydrolysis and a noncomplexing medium with optimum deposition characteristics.

Deposition from the hexachloroplatinate(IV)/buffer solution was performed at –0.2 V vs SCE, the most cathodic potential possible without hydrogen evolution. A rotating glassy carbon electrode was used because of the necessity for an impermeable surface. Other forms of carbon were evaluated and found unsuitable. After deposition, for times of one to ten minutes, a transfer of the glassy carbon electrode with deposited platinum to a pure aqueous 0.05 M sulfuric acid solution prevented interferences from components of the deposition solution and provided an optimum medium for subsequent steps.

An anodic treatment consisting of 2 s at 1.5 V with electrode rotation desorbed and/or oxidized impurities in the deposit, evolved oxygen, and initiated platinum oxide formation. Continued conditioning at 1.25 V for 30 s with rotation and for 90 s without rotation swept away oxygen and completed the oxide formation resulting in maximum platinum electrochemical activity. A cathodic treatment for 10 s at 0.1 V re-reduced the platinum. An anodic potential sweep using differential pulse (DP) voltammetry re-oxidized the deposit and allowed the quantitation of the deposited platinum. The height of the DP peak, centered at +0.85 V, was proportional to the original platinum concentration over the range 0.1 to 50 ppm Pt.

The addition of 0.01 M oxalic acid to the stripping solution extended the concentration range to as low as 10 ppb Pt. Oxalic acid was oxidized at platinum, but not at glassy carbon or platinum oxide, resulting in a DP peak centered at the same potential.

TRACE ELEMENT ANALYSIS OF SERUM FROM BONE MARROW TRANSPLANT PATIENTS USING NEUTRON ACTIVATION ANALYSIS
Order No. DA8429183

BARRETO, EDUARDO MUSSNICH, PH.D. *The University of Florida*, 1984. 123pp. Co-Chairmen: Genevieve Roessler, W. Emmett Bolch, Jr.

Simultaneous analysis of the 7 clinically significant elements Cu, Br, Zn, Co, Se, K and Fe in blood serum was developed using multielement neutron activation analysis (NAA) at the University of Florida Training Reactor (UFTR).

The use of the comparator method eliminated 2 limitations associated with the UFTR: relatively low thermal flux ($1*10^{12}$ neutrons/cm²s) and interrupted operation during night hours.

Hydroxy antimony pentoxide (HAP) resin was successfully employed in the removal of the sample Na (one of the most serious limitations of NAA with regard to samples with a biological matrix) in contrast to recent discouraging literature reports. Tests confirmed Se losses to the resin and sample contamination with Zn leached from plastic syringes.

It was shown that the technique allows for precise and accurate determination of most of the above mentioned elements in the same 3 ml of serum sample.

Blood serum was selected for evaluation in an effort to determine the appropriateness of the intravenous hyperalimentation fluid for maintenance of the nutritional status in a population of bone marrow transplant patients. Serum was sampled weekly during the 6 weeks interval while the 15 patients were fed solely with these fluids.